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(56) Documents cited

GB 1430776 GB 0972943

(58) Field of search

C1A

(54) Extraction of metal ions

(57) A method for extracting metal ions having a high charge and a small ionic radius and in the tetravalent state, from acid liquors involves the step of contacting the liquor with a chelating aminophosphonic acid ion exchange resin, known per se. The method is particularly effective for extracting thorium and other radionuclides from nitric acid raffinates arising during the production of pure uranium for nuclear fuel from uranium ore concentrates. The method can also be applied to the removal of parts per million amounts of actinides such as plutonium, neptunium, protoactinium and uranium from acid liquors destined for disposal or storage.

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Fig. 1.

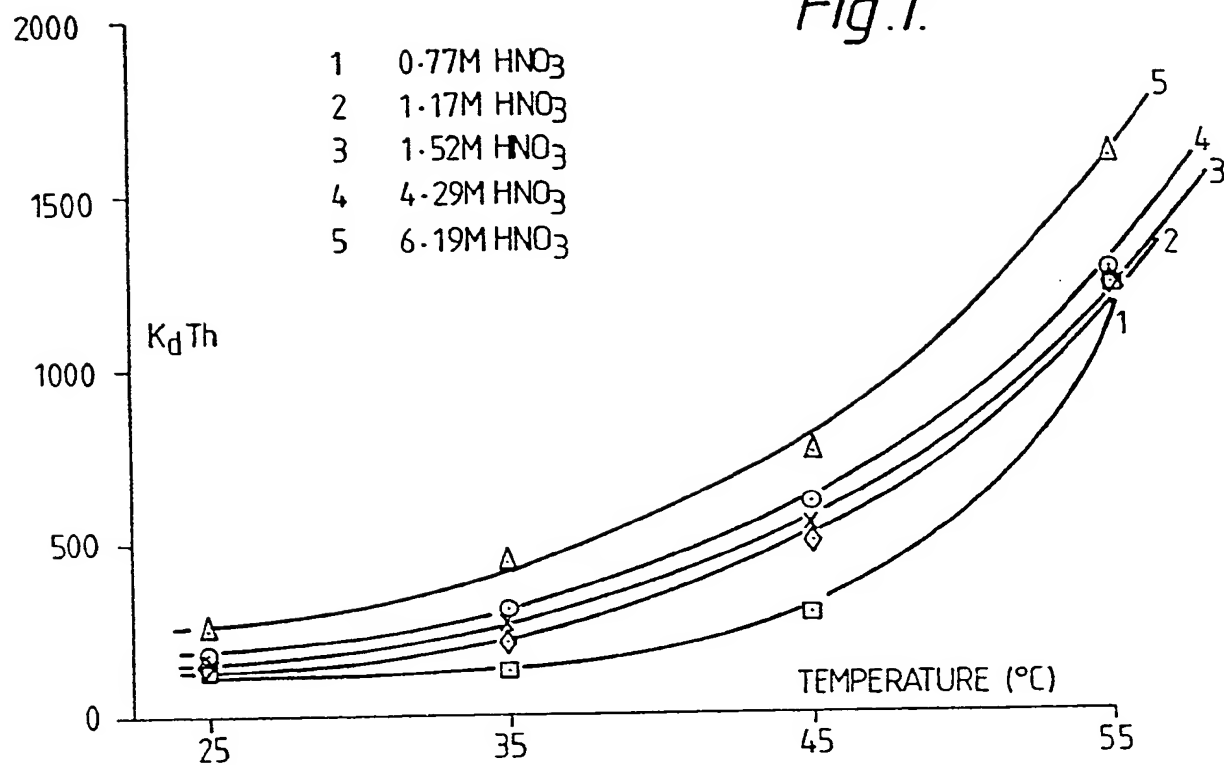
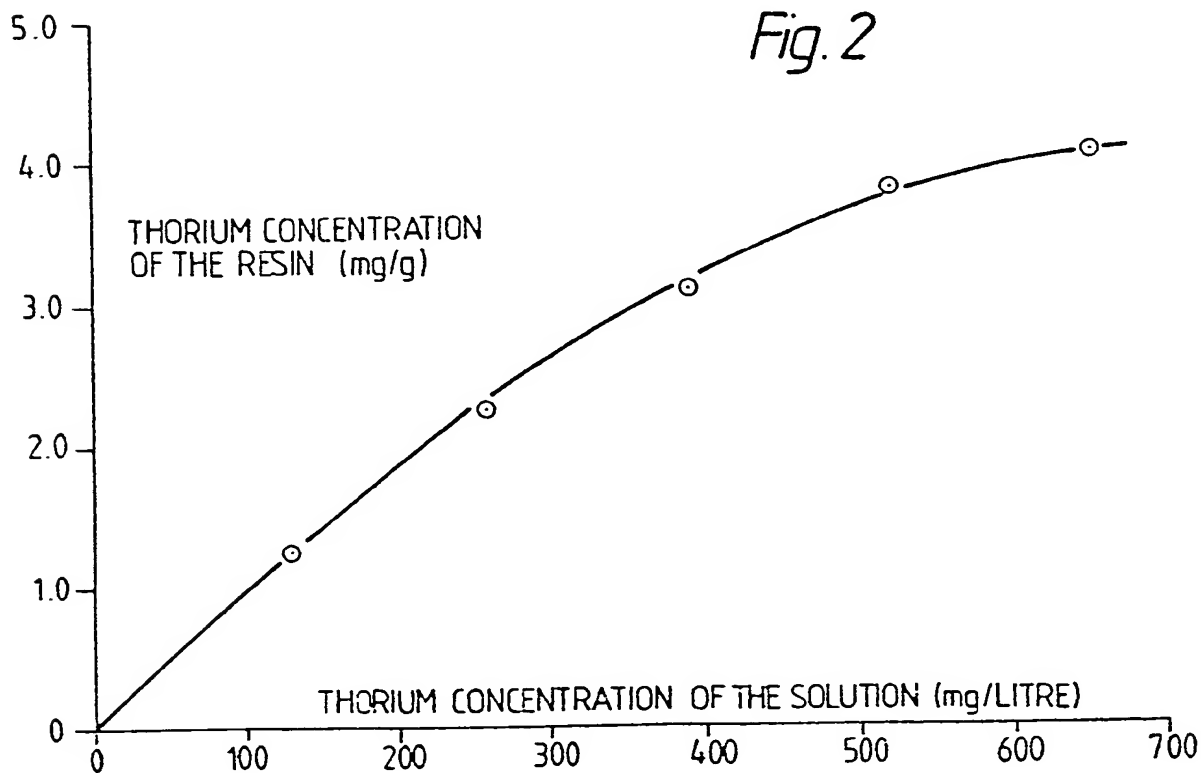


Fig. 2



SPECIFICATION

Extraction of some metal ions from nitric acid liquors

- 5 This invention relates to the extraction of some metal ions from acid liquors. 5
- In the production of nuclear fuel material several sequential processes are necessary to convert uranium ore concentrates to other uranic compounds. In one of these processes the uranium ore concentrate is dissolved in nitric acid and the uranium in the resultant uranyl nitrate liquor is then separated from the impurities which are liberated from the ore concentrate with
- 10 the uranium, predominantly as nitrates. The separation is effected by a solvent extraction procedure from which an acidic raffinate rich in nitric acid but contaminated with the impurities is usually discarded. The major impurities are the alkali and alkaline earth metals, aluminium, some first and second row transition metals, non-uranic radionuclides and various anionic species such as fluorides and sulphates. The radionuclides are principally uranium daughters
- 15 (protoactinium 234 and thorium 234), thorium 230 and the natural thorium isotope Th 232. 15
- The present invention in one of its aspects seeks to remove such radionuclides from the nitric acid raffinate so that, after further treatment, the nitric acid can be recycled to the dissolution process.
- According to the present invention, metal ions having a high charge and a small ionic radius
- 20 and in the tetravalent state can be extracted from acidic liquors by contracting the liquor with a chelating aminophosphonic acid ion exchange resin, known per se. 20
- One example of a metal ion as specified in the preceding paragraph is thorium. Another is protoactinium. The said resin can therefore be employed to remove these radionuclides from nitric acid raffinates as aforesaid. An advantage of a chelating amino-phosphonic acid resin is
- 25 that its ability to absorb thorium and protoactinium from a plant nitric acid raffinate is not normally impaired by nitric acid concentration nor the presence of foreign ions such as sodium, calcium or sulphate. Indeed, it has been established that high nitric acid values (6M) and higher temperatures (of approximately 50°C) can improve the distribution of thorium. This advantage is shown by the results obtained by determining the thorium distribution (KdTh) and the thorium
- 30 capacity of the resin Duolite ES 467 (obtainable from Dia-Prosium Ltd, Hounslow, Middlesex) using a plant nitric acid raffinate of which some of the major constituents are given in the following Table I. 30

TABLE I

Composition of Plant Raffinate

Element	Composition	
40 Nitric acid acidity	9.6% w/v (1.52M)	40
Total Nitrate	11.0% w/v	
Sulphate	0.44% w/v	
Fluoride	0.11% w/v	
Aluminium	880 mg/l	
45 Iron (total)	720 mg/l	45
Calcium	700 mg/l	
Sodium	450 mg/l	
Magnesium	200 mg/l	
Potassium	140 mg/l	
50 Thorium	130 mg/l	50

- Results are depicted graphically in the accompanying Figs. and in Tables II and III. Fig. 1 shows the effect of varying the nitric acid concentration and temperature. Fig. 2 shows the
- 55 effect of thorium concentration. The influence of sodium, calcium and ferric ions on the thorium distribution is indicated in the following Table II and the effect of sulphate concentration in the following Table III. 55

TABLE II

The Effect of Sodium, Calcium and Iron (III) Concentration of KdTh Value

Metal ion in equilibrium with the Resin										
		Na			Ca			Fe		
Initial Metal Ion concentration g/l	0.45	1.2	5.0	0.78	1.9	6.5	0.72	1.8	5.8	
65 KdTh Value	176	162	200	176	212	200	176	70	13	65

TABLE III
The Effect of Sulphate Concentration on Kd Values

5	Initial Sulphate concentration g/l	Fe	Ca	Th	5
	4.4	7	1	176	
	13.0	4	2	171	
10	38.0	2	2	186	10

- For the results in Fig. 1 the nitric acid value of the plant raffinate as received was reduced using the ion-retardation resin AG11-A8 from Bio-Rad Laboratories and increased by the addition of the appropriate quantity of concentrated acid. 10g of the nitric acid pre-conditioned resin was equilibrated at a constant temperature ($\pm 2^\circ\text{C}$) with 100 ml of the appropriate raffinate solutions for 1 hour in a stoppered flask and the distribution values of thorium determined as beta activity, the procedure being carried out at 25, 35, 45 and 55°C . For the results in Fig. 2 10g of preconditioned resin was equilibrated at $25 \pm 2^\circ\text{C}$ with successive 100 ml portions of as received plant raffinate until the beta activity of the equilibrated sample was constant. The beta activity removed was converted to the corresponding thorium value. For the results in Tables II and III appropriate amounts of sodium nitrate, calcium nitrate, ferric nitrate and sulphuric acid were added to portions of the plant raffinate and the procedure followed as for Fig. 1, the temperature being $25 \pm 2^\circ\text{C}$.
- Thorium may be eluted from the resin with 0.5M ammonium carbonate.
- Further examples of metal ions as aforesaid are actinides such as plutonium, neptunium and uranium when in tetravalent state. The employment of a resin as aforesaid is advantageous in its ability to remove small quantities, in the parts per million range, of such metals from waste acidic liquors before discharge or storage.

CLAIMS

1. A method of extraction from acidic liquors of metal ions having a high charge and a small ionic radius and in the tetravalent state, including the step of contacting the liquor with a chelating aminophosphonic acid ion exchange resin, known per se.
2. A method according to claim 1, wherein the acidic liquor is a nitric acid raffinate, and the metal ion for extraction is thorium.
3. A method according to claim 2, including the additional step of eluting thorium from the said resin employing ammonium carbonate.
4. A method according to claim 1, wherein the acidic liquor is a nitric acid raffinate, and the metal ion is or are one or more of the actinides plutonium, neptunium and uranium, all in the tetravalent state and present in the raffinate in concentrations of the order of parts per million.
5. A method of extraction from acidic liquors of metal ions having a high charge and a small ionic radius and in the tetravalent state, substantially as herein described.